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INTENSITY OF COLORING IN CERAMICS WITH GLAUCONITE ADDITIVES

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The possibility of using glauconite additives in ceramic production and their effect on the intensity of ceramic tinting is investigated. It is found that the effect of glauconite additive on the color of fired articles depends on the composition of clay, the amount of the additive, its specific surface area, and firing conditions: the rate of temperature rise, the maximum temperature, and the firing duration.

The purpose of this study is to investigate the possibility of using glauconite as a coloring additive in ceramic production. The non-worked deposits of glauconite in Lithuania comprise about 1 billion tons. Other neighboring countries are also rich in glauconite resources. Mineral glauconite in natural conditions is mixed with other hydromicas, montmorillonite, or quartz. The study of the possibility of using glauconite in the production of mineral paints, in softening water or purifying it from heavy metals, in the production of fertilizers, etc. is still at the experimental level. Furthermore, glauconite is of interest as an iron-rich local additive for ceramic production. It is believed that glauconite additives may influence the intensity of a red tint in ceramics and decrease the sintering temperature.

Iron oxides in firing impart a red tint to ceramics, as a consequence of the formation of hematite Fe_2O_3. In the presence of a substantial quantity of $CaCO_3$ calcium pyroxenes are formed in clay, as well as melilite which imparts a yellow or dark yellow color to the ceramic base [1, 2]. The content of iron oxides in local clays used in the production of construction ceramics reaches 6 – 7%, the content of CaO — around 10%, MgO — 3% (contained in carbonates $CaCO_3$ and $MgCO_3$). Ceramic articles based on locals clays have a light red shade. There is a high demand for building ceramics (facing brick, roof tile) of bright red or brown colors. Such products can be produced from local clays only by means of iron-bearing additives [3 – 8] (pigments, industrial waste, natural minerals), of which glauconite is one of the most available and inexpensive additives.

In our experiments we used glauconite from the Merkis and Shventoi deposits, as well as clay from the Girininkai deposit (Lithuania) and Veselovskoe clay (Ukraine). The compositions of the materials are listed in Table 1.

The clay from the Girininkai deposit is a hydromica clay with a prevalence of muscovite and illite minerals. Other minerals that have been identified include kaolinite, quartz, dolomite, and feldspar. Veselovskoe kaolinite clay containing insignificant quantities of iron and calcium oxides was used to compare the effect of glauconite additives on the color of ceramics. Kaolin and quartz prevail in the mineralogical composition of this clay. The glauconite rock, in addition to mineral glauconite, also contains quartz and hydromica (muscovite and illite). It is established that natural glau-

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TABLE 1

Material	Weight content, %							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	calcination loss
Clay from deposits:								
Girininkai	47.69	13.36	6.19	9.05	0.06	3.59	0.96	11.78
Veselovskoe	59.50	25.20	1.52	0.45	–	0.60	0.30	8.60
Glauconite from deposit:								
Merkis	64.09	6.68	11.16	2.15	0.01	2.05	0.68	5.50
Shventoi	48.52	6.80	12.86	9.89	0.01	2.05	0.62	6.86

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conites by their granulometric composition are nondispersed materials (the content of argillaceous particles is below 20%).

Dried glauconite was used in its natural form (the specific surface area of Shventoi glauconite determined on a PSKh-4 instrument was 50 m^2/kg, that of Merkis glauconite was 110 m^2/kg) or milled in a porcelain mill to a specific surface area of 250 ± 10 and 350 ± 10 m^2/kg. The technological properties of glauconites are given in Table 2.

To investigate the effect of additives on the color of ceramics, we prepared samples from clay mixtures with a gradually increasing (from 0 to 50%) content of additives. Dried samples were fired in a SNOL-1.6, 2.51/11-U3 laboratory furnace in varying firing conditions: the temperature rise rate, the maximum temperature, and the firing duration. We use two rates of temperature rise: a medium rate (500 K/h) and a slow rate (200 K/h). The firing temperatures were 1000, 1025, and 1050°C, and the duration of the isothermal exposure was 0.5, 1, 2, and 4 h.

The x-ray phase analysis of materials was performed on a DRON-6 instrument with a copper anode.

The color of the samples was measured using a Spectraflash SF450X spectrophotometer with illumination D 65 10 Deg. We determined the luminosity (whiteness) L of samples using a graduation scale from 0 (black) to 100 (white); color parameters: a) on the axis from green ($-a$) to red ($+a$), b) on the axis from blue ($-b$) to yellow ($+b$); L, a, and b were measured in the NSB units (National Bureau of Standards).

The study of the effect of glauconite additives on properties of molding mixtures indicated that natural glauconite behaves as a grog additive. The effect of glauconite additives on the color of ceramics depends on the clay composition, the quantity of the additive, its surface area, and the firing procedure. The glauconites considered are not intensely coloring additives. The tint of ceramic samples becomes significantly modified only when the content of the additive in a molding mixture grows to 30% (which is equivalent to a total amount of 7.69% Fe_2O_3 in the mixture based on Girininkai clay with Shventoi glauconite and to 4.40% Fe_2O_3 in the case of Veselovskoe clay). It is established that the content of 5.6 – 6.4% Fe_2O_3 in molding mixtures based on Veselovskoe clay is sufficient for adequate tinting of ceramics.

A ceramic sample based on Veselovskoe clay (without additives) fired at a temperature of 1000°C for 4 h has a yellowish-white color ($L = 81.86$, $a = 7.71$, $b = 17.08$). As natural glauconite from the Shventoi deposit is added up to 20%, the color of the ceramic sample is not bright. Increasing the additive to 30% produces saturation of color and yields a reddish-brown tint. As the additive content grows from 0 to 50%, the color parameters of the sample vary significantly: L varies from 81.86 to 56.64 (i.e., 1.5 times), a from 7.71 to 15.78 (2 times), and b from 17.08 to 25.55 (1.5 times). The x-ray phase analysis indicates that the glauconite additive in the molding mixture based on Veselovskoe clay leads to the formation of hematite that is responsible for the color of ceramics (Fig. 1). As the amount of the additive grows, the content of hematite increases and the color is intensified (Figs. 2 and 3).

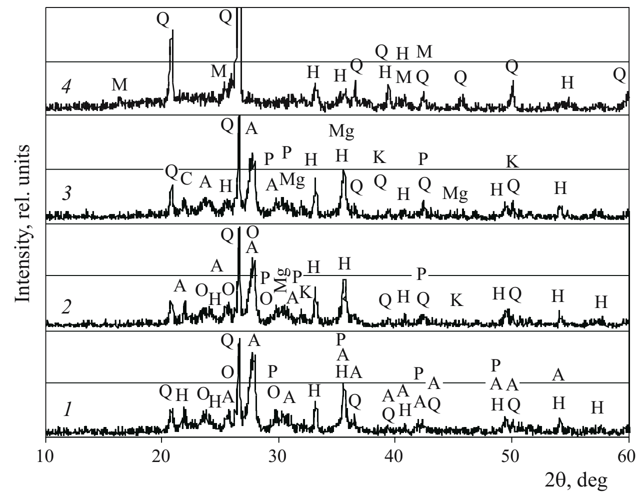

Fig. 1. X-ray samples made of molding mixtures with Shventoi glauconite additives fired at 1000°C for 4 h: *1*) Clay from Girininkai deposit and 10% natural glauconite (50 m^2/kg); *2*) the same, 30% natural glauconite (50 m^2/kg); *3*) the same, 30% milled glauconite (350 m^2/kg); *4*) Veselovskoe clay and 30% milled glauconite (350 m^2/kg); Q) quartz; A) anorthite; M) mullite; H) hematite; Mg) magnesium ferrite; O) orthoclase; K) potassium and iron-bearing oxides; P) augite.

A ceramic sample based on clay from the Girininkai deposit (without additive) fired at a temperature of 1000°C for 4 h has a pale red color ($L = 57.13$, $a = 21.29$, $b = 25.98$). The color intensity of the samples based on the same clay with a 20% natural glauconite additive decreases. The diffraction patterns of these samples shows the formation of potassium-bearing feldspar (orthoclase) and pyroxene (augite) containing iron in their structure, as a consequence of which the color intensity of ceramics decreases. A further increase in the content of the additive up to 30% and more decreases

TABLE 2

Parameter	Glauconite from deposit	
	Merkis	Shventoi
Plasticity number	8.69	4.49
Moisture, %:		
molding	20.18	19.85
critical	7.05	7.95
Drying sensitivity coefficient	1.59	2.54
Shrinkage in drying, %	6.10	4.69
Properties of fired samples*:		
density, kg/m^3	2009 (1982)**	2100 (2092)
bending strength, MPa	6.87 (7.35)	10.02 (11.36)
color	Dark brown	Reddish-brown

* Firing for 4 h at 1000°C.

** Figures in brackets are the results of analysis of samples based on glauconite milled to specific surface area of 350 m^2/kg.

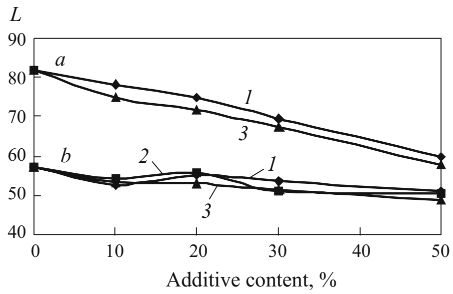

Fig. 2. The effect of glauconite additives from the Shventoi deposit and its specific surface area on the luminosity *L* of samples based on Veselovskoe clay (*a*) fired at 1000°C for 2 h and Girininkai clay (*b*) fired at 1000 for 4 h.

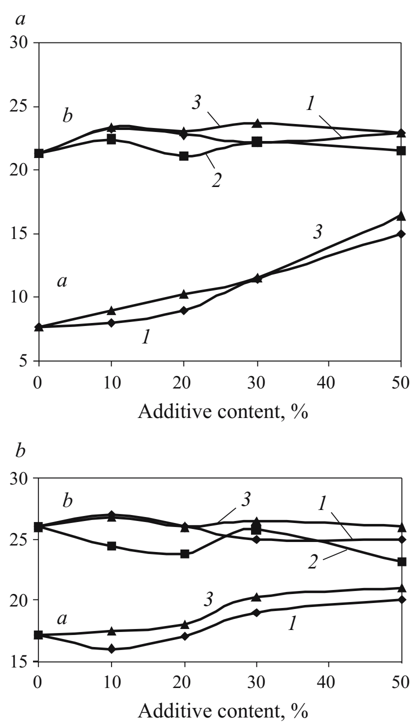

Fig. 3. The effect of glauconite additive from Shventoi deposit and its specific surface area on color parameters *a* and *b* of samples based on Veselovskoe clay (*a*) and Girininkai clay (*b*). Notations and firing schedules same as in Fig. 2.

the quantity of orthoclase and leads to the formation of colorant compounds: iron oxide and magnesium ferrite (of red color) which gives a more intense color to the samples (Fig. 1, curves *2* and *3*). As the glauconite additive content grows from 0 to 50%, the color parameters vary: *L* from 57.13 to 48.73, *a* from 21.29 to 22.84, and *b* from 25.98 to 25.75.

The use of clays of different compositions demonstrates that the additives have a more perceptible effect on the color of samples based on the Veselovskoe clay. An additive of Shventoi glauconite containing a higher content of Fe_2O_3 has a more pronounced effect on ceramics tinting than an additive of Merkis glauconite. The color of fired samples depends not only on the quantity, but also on the specific surface area of the additive. As the specific surface area grows, the intensity of the red color in ceramic increases (Figs. 2 and 3).

A comparison of ceramic samples containing 30% Shventoi glauconite with a specific surface area of 50 and 350 m^2/kg shows that the increased surface area leads to the formation of magnesium ferrite, increases the quantity of hematite, and results in the disappearance of orthoclase; as a consequence, the color intensity of ceramics increases (Fig. 1, curves *2* and *3*).

The intensity of the color of samples based on molding mixtures of identical compositions depends on the firing conditions: the rate of the temperature rise, as well as firing duration. As the maximum firing temperature increases from 1000 to 1050°C and the isothermal exposure extends from 0.5 to 4 h, the color intensity grows.

This, the effect of glauconite additives on the color of ceramics depends on the composition of clay, the quantity of the additive, its specific surface area, and the firing conditions. The intensity of red tinting depends not only on the absolute quantity of iron-bearing compounds contained in the molding mixture, but also on the composition of emerging iron-bearing compounds: as the quantity of newly formed colorant compounds grows (hematite, etc.), the intensity of the color of ceramics increases, whereas when the amount of other compounds with iron incorporated in their structure grows (orthoclase, augite, etc.), the color intensity decreases.

The obtained results have been used to issue recommendations for using glauconite additives in the production of roof tiles.

REFERENCES

1. R. Kreimeyer, "Some notes on the firing colour of clay bricks," *Appl. Clay Sci.*, **2**, Issue 2, 175 – 183 (1987).
2. J. Molera, T. Pradels, and M. Vendrell-Saz, "The colours of Ca-rich ceramic pastes: origin and characterization," *Appl. Clay Sci.*, No. 13, 187 – 202 (1998).
3. B. I. Musienko, I. I. Stavnitser, and M. V. Shabanov, "Utilization of industrial galvanic waste in ceramic pigments," *Stroit. Mater. Konstr.*, No. 1, 30 – 32 (1994).
4. I. A. Al'perovich, G. I. Bozh'eva, and V. A. Kryukov, "The implementation of production technology of bulk-tinted ceramic brick," *Stroit. Mater.*, No. 1, 2 – 6 (1993).
5. I. A. Al'perovich, "Innovations in technologies of bulk-tinted ceramic facing brick," *Stroit. Mater.*, No. 7, 5 – 9 (1993).
6. S. A. Komissarov, T. M. Korchuganova, and A. V. Belyakov, "Construction materials using leather production waste," *Steklo Keram.*, No. 1, 20 – 21 (1994).
7. F. Andreola, L. Barbieri, A. Corradi, et al., "Utilisation of municipal incinerator grate slag for manufacturing porcelainized stoneware tiles," *J. Eur. Ceram. Soc.*, **22**, 1457 – 1462 (2002).
8. F. Bondioli, A. M. Ferrari, C. Leonelli, T. Manfredini, "Syntheses of Fe_2O_3/silica red inorganic inclusion pigments for ceramic applications," *Mater. Res. Bull.*, **33**(5), 723 – 729 (1988).